

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 23/10, C08J 5/18, C08F 210/06	A1	(11) International Publication Number: WO 95/32242 (43) International Publication Date: 30 November 1995 (30.11.95)
(21) International Application Number: PCT/US95/06576		(81) Designated States: CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 24 May 1995 (24.05.95)		
(30) Priority Data: 08/248,120 24 May 1994 (24.05.94) US		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US).		
(72) Inventors: McALPIN, James, John; 16811 Heath Hollow, Houston, TX 77058 (US). MEHTA, Aspy, Keki; 5611 Forest Timbers, Humble, TX 77346 (US). STAHL, G., Allan; 8111 Hurst Forest, Humble, TX 77346 (US). AUTRAN, Jean, Philippe; 74, rue Camille Lemonnier, B-1060 Brussels (BE).		
(74) Agents: MILLER, Douglas, W. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		

(54) Title: ARTICLES MADE FROM POLYPROPYLENE, HIGHER α -OLEFIN COPOLYMERS

(57) Abstract

Articles made from propylene, α -olefin copolymer, where the α -olefin has 5 or more carbon atoms, made with a metallocene catalyst system, provide substantially higher cold flow resistance than propylene copolymers made from α -olefins having 4 or fewer carbon atoms. Other properties such as ultimate tensile strength and impact strength are substantially higher as well. Such polymers can be used to advantage in flexible films, tubing, fibers, fabrics, oriented films, extruded profiles, molded parts, and sheets.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

APPLICATION FOR PATENT

TITLE: Articles Made from Polypropylene, Higher α -olefin Copolymers

TECHNICAL FIELD

This invention relates generally to films, sheets, molded articles, oriented fibers, oriented films, extruded profiles, tubing and other articles made from propylene α -olefin copolymers. The articles exhibit exceptional physical properties, including relatively low cold flow or creep. More specifically this invention relates to the use of certain propylene α -olefin copolymers (formed utilizing a metallocene catalyst system) where the α -olefin is selected from α -olefins having 5 or more carbon atoms.

BACKGROUND

Polyolefin polymers are well known articles of commerce. The uses of polyolefins are many and well known to those of skill in the art. Polyolefins have many useful physical properties. However, most polyolefins display unacceptable cold flow properties, that is, at room temperature or service temperature, they exhibit flow when subjected to low levels of stress for an extended period. Cold flow resistance is a property of importance in many polymer applications. Cold flow is defined as the non-recoverable deformation of a polymeric article in response to a force or stress (well below the yield stress of the material), applied for an extended time at a selected temperature. Different polymers will exhibit different resistances to cold flow.

Polypropylene homopolymers and copolymers have come into wide use. Over 5 million tons (4 million metric tons) of polypropylene are manufactured each year in the United States alone. Polypropylene has a wide range of commercial uses, from packaging films and sheeting to molded food containers and fibrous constructions employed in diapers and hospital gowns.

There are several classes of polypropylene. One of these classes is statistical copolymers of propylene and another α -olefin, sometimes also known as random copolymers. In the past this class has tended to be represented largely by

- 2 -

copolymers of propylene and ethylene, usually made using Ziegler-Natta catalysts. Copolymerization of higher α -olefins (HAO) (those α -olefins of 5 or greater carbon atoms) with propylene, using Ziegler-Natta catalysts has been problematic in the past due to the lower reactivity of these catalysts towards higher α -olefins. The Ziegler-Natta catalyzed ethylene copolymers have generally found use based on their substantially different properties when compared to polypropylene homopolymers. Broadly, the differences between Ziegler-Natta catalyzed homopolymers and propylene-ethylene copolymers are seen in such properties as lower melting point, greater flexibility, better clarity and slightly improved toughness for the copolymer.

EP 0 495 099 A1 to Mitsui Petrochemical Industries discloses a method for polymerization of the propylene α -olefins utilizing metallocene-alumoxane catalyst systems. The document also discloses a propylene α -olefin copolymer where the propylene is present from 90-99 mole % and the α -olefin is present from 1-10 mole %. This document discloses that the propylene α -olefin copolymers would have a narrow molecular weight distribution (M_w/M_n), the copolymer would have a low melting point, and the copolymers have excellent softness. The document also discloses a straight line relationship between T_m and propylene content, however, no distinction is drawn to the melting point depression effect of different α -olefins.

EP 0 538 749 A1 to Mitsubishi Petrochemical Co. discloses a propylene copolymer composition to produce a film having excellent low-temperature heat sealing, where the composition has 1 to 70 wt% of A and 30-99 wt% of B where:

A is a propylene ethylene or α -olefin copolymer where the α -olefin has 4-20 carbon atoms and a M_w/M_n of not more than 3.

B is a propylene ethylene or α -olefin copolymer where the α -olefin has 4-20 carbon atoms and a M_w/M_n of 3.5 to 10.

Copolymer A is polymerized by a metallocene catalyst system.

Copolymer B is polymerized by a Ziegler-type catalyst.

Substantially all examples utilize propylene-ethylene copolymers or propylene homopolymers.

EP 0 318 049 A1 to Ausimont discloses crystalline copolymers of propylene with minor portions of ethylene and/or α -olefins. The copolymers are disclosed to have very good mechanical properties. The copolymers are polymerized in the presence of methyalumoxanic compounds. The examples of this document show propylene-ethylene and propylene-1-butene copolymers.

Among the polymers that demonstrate acceptable cold flow resistance are

- 3 -

polyvinyl chloride (PVC). The cold flow resistance of PVC enables it to be used in applications where the relatively poor cold flow of polyolefins would be unacceptable.

Fresh meat wrap is an example of the deficiency of polyolefins when compared to PVC. PVC films are known and valued for their ability to "snap back" after deformation. This snap-back attribute is directly related to the film's ability to resist cold flow. In retail meat displays, such deformation would be caused when the packaged meat is handled. Because of its "snap back", meat wrapped in PVC film, even after handling, does not show the effects of such handling. Polyolefins have repeatedly been tried in film applications such as meat wrap with little commercial success, because when deformed by handling, a polyolefin's tendency to cold flow leaves unacceptable finger marks or other depressions or distortions of the film even after the packaged meat itself has recovered (or substantially resumed the shape it had before deformation). Polypropylene and polyethylene of the polyolefins especially exhibit this deficiency, due to their relatively poor cold flow.

However, even though PVC has many advantages in applications as discussed above as well as many others, PVC has several substantial drawbacks that have made its replacement by other plastics, such as polyolefins, a high priority in many of those applications. As a first example of a drawback, the density of PVC is substantially higher than most polyolefins. The density of most PVC is about 1.2 g/cc versus a density well below 1.0 g/cc for most polyolefins. This has a very practical effect, that a given unit of weight of PVC will yield substantially less product than a unit of polyolefin. A second drawback of PVC is that upon combustion, for example in waste or trash incineration, PVC will evolve hydrochloric acid. Still another drawback, especially for food and medical related PVC applications, is the extractability of plasticizers such as phthalate esters used in flexible PVC.

In other articles, such as fibers and fabrics, polyamides, polyesters and other such thermoplastics may be used in applications that are substantially foreclosed to polyolefins, such as apparel and fiber yarns due to the polyolefin's relatively poor cold flow. In apparel, the cold flow resistance and "drape" or "hand" of polyolefins is generally deficient to that of other thermoplastics, for instance, a polyamide or polyester. The cold flow resistance of conventional polyolefins is noticeably defensive to the thermoplastics discussed above. Polyolefins in applications such as hosiery would show deformation after normal

- 4 -

body movement leading to an undesirable baggy look.

In molded articles, shape is often a critical parameter. Cold flow due to a contained load or due to an applied exterior or interior force could cause unacceptable deformation in a molded part. Additionally, much less weight and time would be necessary to cause a load-set or deformation due to a static load such if the molded parts were fabricated from most conventional polyolefins.

More recently, a class of compounds having properties between those of cured rubbers and soft plastics have been investigated. These compounds are generally referred to as thermoplastic elastomers (TPE). The classical TPE structure involves a matrix of an uncured elastomer such as, for example, a polybutadiene, polyester or polyurethane, tied together by thermoplastic junction regions. A well known example of a TPE is Shell's Kraton ® G, a triblock of styrene and hydrogenated polybutadiene, where the thermoplastic crosslinking points are small domains of glassy polystyrene joined by rubbery polybutadiene blocks. This structure leads to behavior similar to vulcanized elastomers at ambient temperature but, at temperatures above the polystyrene softening point, the system undergoes plastic flow.

A subset of thermoplastic elastomers, embodying only olefin based polymers, is referred to as thermoplastic olefins (TPO). A typical TPO comprises a melt blend or like mixture of one or more thermoplastic polyolefin resins with at least one olefin copolymer elastomer (OCE). The thermoplastic polyolefin resin (usually a polypropylene) will give the TPO rigidity and temperature resistance while the elastomer imparts flexibility and resilience as well as improving the toughness of the material.

TPOs find particular application in the auto industry for flexible exterior body parts such as, for example, bumper covers, nerf strips, air dams and the like. In such applications, it is desired that the TPO have good resiliency (ability of the part to return to its original shape after deformation), impact strength at low temperatures, flexibility, high heat distortion temperature, surface hardness and surface finish characteristics. Additionally ease of processability and molding is desired.

Other application for TPOs include films, footwear, sporting goods, electric parts, gaskets, water hoses and belts, to name just a few. Particularly in films, elasticity and clarity properties are important. Other of the aforementioned properties will be important depending upon the desired application.

However, TPOs suffer compared to TPEs such as Kraton G due to the

- 5 -

inability of the polypropylene matrix to resist stress over relatively long periods of time, and the TPOs defensive toughness or impact strength.

Polymer compositions such as TPEs exhibit cold flow resistance and resiliency that generally substantially exceeds that of TPOs. This cold flow resistance and resiliency enables TPEs to be used in applications where the relatively poor cold flow and resiliency of polyolefins would be unacceptable. Such applications include molded articles for automobiles and applicances. In molded articles, shape is often a critical parameter. Cold flow due to a contained load or due to an applied force could cause unacceptable deformation in a molded part. Additionally, much less weight and time would be necessary to cause a load-set or deformation due to a static load such if the molded parts were fabricated from most polyolefins rather than TPOs. Versus TPEs, the performance of most polyolefins would be even poorer.

Even though TPEs have many advantages as discussed above, their cost makes them unacceptable for some applications and marginally acceptable in others. Though much less expensive, TPOs on the other hand have not been an ideal choice either, due to the above mentioned physical properties.

There is therefore a need for a polyolefin, specifically a polypropylene copolymer that will resist cold flow to a sufficient extent that it could replace PVC, conventional polyolefins, or improve the properties of thermoplastic olefin compositions in many applications.

SUMMARY OF THE INVENTION

It has been discovered that propylene copolymers made utilizing metallocene catalysts to polymerize propylene with α -olefin comonomers having 5 or more carbon atoms (higher α -olefins (HAO)), show a surprising enhancement in important physical properties when compared to propylene copolymers utilizing α -olefins of 4 carbon atoms or less (for purposes of this application this classification includes ethylene). In an embodiment of the present invention, the most striking step change is evidenced in cold flow or creep resistance values and the effect of these values on articles made from materials according to this embodiment.

In an embodiment of the present invention, extruded, molded and calendered articles such as film, tubing, fibers, oriented films, extruded profiles, molded parts, sheets, or other fabricated articles are comprised of a copolymer of propylene and at least one HAO. The HAO is present in the copolymer in the range

of from 0.2 to 6 mole percent based on the total moles of the copolymer. The copolymer will have a $M_w/M_n \leq 5$ and a peak melting point (DSC) in the range of from 100° C to 145° C. An article made from these copolymers or their compounds can exhibit improved creep or cold flow resistance when compared to articles based on propylene-ethylene copolymers.

Articles made from propylene-HAO copolymers will be particularly useful in applications where minimizing cold flow or creep is important.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings where: Fig. 1 shows the effect of comonomer on melting point depression in a propylene copolymer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention concerns certain classes of fabricated polypropylene articles, and their uses. These articles have unique characteristics which make them well suited for use in certain applications. Flexible films, tubing, sheets, fibers, oriented films, extruded profiles, molded articles and other articles made therefrom, have superior cold flow (creep) resistance compared to articles made from polypropylene-ethylene copolymers. A detailed description follows of certain preferred resins for use in fabricating articles that are within the scope of our invention, and preferred methods of producing these resins and their products.

Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of the invention. For example, though the properties of films, fibers, fabrics, and molded articles are used to exemplify the attributes of the copolymers, the copolymers have numerous other uses. To the extent that our description is specific, this is solely for the purpose of illustrating preferred embodiments of our invention and should not be taken as limiting our invention to these specific embodiments.

The term random or statistical copolymer as used herein shall mean copolymers of propylene and other α -olefins polymerized in a medium which the contents of the various comonomers and other process conditions are maintained substantially constant throughout the course of the reaction. Variations in the composition of the resulting copolymers due to the existence of chemically distinct sites within the catalytic entity from which they are prepared or to normal

- 7 -

variations experienced in sequenced reactors, as long as the resulting "reactor blend" polymers are miscible in the melt, are accepted in the current definition.

We have discovered that certain metallocene catalyst systems can be used to polymerize propylene statistical resins having properties which are highly desirable for conversion into various products. Generally these resins are isotactic polypropylene statistical copolymers and homopolymers, the copolymers utilize propylene and one or more alpha-olefins. For purposes of this application, the term isotactic is intended to mean a polymer where propylene tacticity distribution will be greater than about 90 percent mmmm pentads, where m is a meso diad, (m is defined as the same relative configuration of methyl groups of two successive monomer units (diad) to each other), preferably in the range of from 94 to 98 percent mmmm pentads, most preferably in the range of from 95 to 97 percent mmmm pentads, as determined by nuclear magnetic resonance (NMR).

Production of the Resins

The polypropylene copolymers of the present invention are preferably produced using supported metallocene catalysts. The copolymers may be produced in many types of reactors or reaction schemes, including, but not limited to, fluidized bed or stirred bed gas phase reactors, slurry or bulk liquid reactors of tank or loop type, or any other process practiced for the polymerization of polypropylene. Series bulk liquid boiling propylene pool reactors are preferred.

Specific metallocene-type catalysts are known to be useful for producing isotactic olefin polymers and may be found in EPA 485 820, EPA 485 821, EPA 485 822, EPA 485 823, by Winter, et al. and US 5,017,867 by Welborn. These publications are incorporated by reference in the present application for the purposes of U.S. patent practice.

Various publications describe placing catalyst systems on a supporting medium and use of the resulting supported catalysts. These include U.S. Patent Numbers 5,006,500, 4,925,821, 4,937,217, 4,953,397, 5,086,025, 4,912,075, and 4,937,301 by Chang and U.S. Patent Numbers 4,808,561, 4,897,455, 5,077,255, 5,124,418, and 4,701,432 by Welborn, all of which are included in the present application by reference for purposes of U.S. patent practice.

Specific information on the use of support techniques for metallocene-type catalysts for use in the preparation of propylene α -olefin polymers may be found in U.S. patent 5,240,894 by Burkhardt, which is also incorporated by reference for purposes of U.S. patent practice. While catalysts used for the following examples

were employed in a bulk liquid-phase polymerization, catalysts for commercial use may be used in other processes including for example, gas phase and slurry processes.

Resins produced by the above referenced processes and catalysts will incorporate α -olefin comonomers in the range of from 0.2 mole percent to 6 mole percent based on the total moles of the copolymer. Above 6 mole percent, the resulting resin will make an article with a melting point too low for many preferred applications. Below 0.2 mole percent comonomer, the flexural modulus becomes too high, leading to a product that is too stiff for many applications. In a more preferred embodiment, the α -olefin comonomer is in the range of from 0.5 to 3 mole percent. In the most preferred embodiment, the α -olefin is present in the range of from 1 to 3 mole percent.

In one preferred embodiment, the catalyst system comprises a silicon bridged bis (substituted 2-methyl-indenyl) zirconium dichloride or a derivative thereof, methyl alumoxane and an inorganic support. In a more preferred embodiment, dimethyl silyl bis (2-methyl-benzindenyl) zirconium dichloride is the metallocene of choice. This preferred catalyst system was used to generate the propylene-ethylene and propylene-hexene resins used in the films whose properties are shown in Table 1. However, it would be possible to copolymerize any α -olefin of 2 to 20 carbon atoms utilizing these and similar catalyst systems. Further details regarding preparation of the catalyst system and production of the resin are provided in the examples that follow.

Characteristics of the Resins

In a preferred embodiment, the copolymers are isotactic in nature. The polymers will generally have a narrow molecular weight distribution, as characterized by the M_w/M_n (weight average molecular weight/number average molecular weight) (molecular weight distribution MWD), ≤ 5 . Preferably ≤ 3.5 , more preferably ≤ 3.2 , most preferably ≤ 3.0 , and the most preferred ≤ 2.5 . M_w/M_n (MWD) is determined by Gel Permeation Chromatography (GPC), as is molecular weight. Such techniques are well known. The techniques are described in copending application USSN 08/164,520 incorporated herein by reference for purposes of US patent practice. The polymers will exhibit melting points in the range of from 100° C to 145° C, more preferably, in the range of from 110° C to 135° C, most preferably in the range of from 115° C to 135° C.

Food law compliance can be an important criterion for articles made from

these resins, such compliance usually directly affected by the extractable content of an article made from a resin. A standard of U.S. Food and Drug Administration as noted in 21 CFR § 177.1520 is to use the n-hexane reflux procedure, the maximum extractables level of the products of the present invention is expected to be less than 5 wt%, preferably less than 4 wt%, most preferably less than 3 wt%.

Useful melt flow rates of the polymers of the present invention are in the range of from 0.1 to 5000 dg/min. In a preferred embodiment, the melt flows are in the range of from 0.5 to 5000 dg/min. In a most preferred embodiment, for films and molded articles the melt flow rates are in the range of from 1 to 10 dg/min. In a preferred embodiment for fibers and fabrics the melt flow rates are in the range of from 10 to 3000 dg/min. Melt flow rates are measured by ASTM D-1238 condition L.

Making a Film, Tubing, or Sheet

Films may be made by any techniques known by those of ordinary skill in the art. For example, blown films produced with an annular die and air cooling, or cast films using a slot die and a chill-roll for cooling are both acceptable techniques. Oriented films may be produced by either post extruder manipulation of the blown film through heating and orientation, or by longitudinal stretching of an extruded sheet followed by tentering techniques. Films are generally in the range of from 0.2 to 10 mils (5.08 to 254 µm).

Sheet may be made either by extruding a substantially flat profile from a die, onto a chill roll, or alternatively by calendering. Sheet will generally be considered to have a thickness of from 10 mils to 100 mils (254 µm to 2540 µm), although sheet may be substantially thicker. Films or sheets for test purposes may be made by compression molding techniques, as well.

Tubing may be obtained by profile extrusion. For use in medical applications or the like, the tubing will generally be in the range of from 0.31 cm (1/8") to 2.54 cm (1") in outside diameter, and have a wall thickness of in the range of from 254 µm (10 mils) to 0.5 cm (200 mils).

Films made from the products of a version of the present invention may be used to contain food articles such as meat and snacks for instance. Such films may also be used to protect and display articles of apparel.

Sheet made from the products of an embodiment of a version of the present invention may be used to form containers. Such containers may be formed by thermoforming, solid phase pressure forming, stamping and other shaping

- 10 -

techniques may be used for foods such as meat or dairy products. Sheets may also be formed to cover floors or walls or other surfaces.

Tubing made from the products of this invention may be used in medical, food, or other uses that will be apparent to those of ordinary skill in the art.

Making a Molded Article

Molded articles may be made by any techniques known to those of ordinary skill in the art. For example, molded articles may be fabricated by injection molding, blow molding, injection blow molding, extrusion blow molding, rotational molding, or foam molding. Molded parts are found in many thicknesses, however 508 μ m thicknesses or greater predominate.

Properties of Molded Articles and Extruded Profiles Produced from the Resins

The resins discussed above, when formed into molded articles, will show superior properties when compared to either commercially available polypropylene homo or copolymer products or to metallocene catalyzed propylene ethylene or α -olefin copolymer resins where the α -olefin has 4 carbon atoms or less.

Prospective example 8 indicates that molded parts will show improved physical properties in the comparison noted above.

Determination of R_{ma}

A parameter useful for defining cold flow or creep resistance is a value known as compliance. For purposes of this application, compliance is defined as the amount of strain observed on an article, that is placed under a specific stress for a specified time divided by the magnitude of the stress. Those of ordinary skill in the art will recognize that the stress should be below the specimen's yield stress.

A useful technique for evaluating the step change in properties between propylene-HAO copolymers and propylene-ethylene copolymers (both metallocene catalyzed) has been developed.

For films, molded articles, tubing, sheets, and similar articles, the technique uses the quotient of the compliance of a propylene-HAO copolymer, divided by the compliance of a propylene-ethylene copolymer.

The quotient is the symbol R_{ma}, where:

- 11 -

$$R_{ma} = \frac{\text{Compliance of propylene-HAO copolymer article}}{\text{Compliance of propylene-ethylene article}}$$

where the resins to form each article are chosen such that the tensile modulus of each article is substantially the same as that of the other article.

In the determination of R_{ma} , it is important that substantially all parameters that affect the physical properties of the articles in both the numerator and denominator of the factor be the same.

Such factors include, but are not limited to:

for the resins: molecular weights should vary by no more than 10%

for the fabricated article: fabrication conditions and techniques;

dimensions of the test specimen;

post fabrication treatments;

blend components; or additives

It will be understood by those of ordinary skill in the art that comonomer content of either HAO or ethylene can be varied for purposes of attaining substantially the same tensile modulus in both the propylene-HAO and propylene-ethylene copolymers.

The choice of equal tensile modulii for the articles of both numerator and denominator ensures that the comparison is made at a constant degree of flexibility of the articles. Articles made from isotactic propylene-HAO copolymers of the present invention will have a R_{ma} exceeding 1.1, indicating significantly improved resistance to cold flow compared to the statistical propylene-ethylene copolymers. Blends of olefin polymers, wherein at least one polymer is a statistical isotactic propylene-HAO copolymer are also contemplated as long as the R_{ma} of the article is greater than 1.1. Possible blend materials may include, but are not limited to; ethylene copolymers of ethylenically unsaturated esters, polyethylene homopolymers and copolymers with α -olefins, polypropylene homo and copolymers, ethylene propylene rubbers (EP), ethylene, propylene, diene monomer elastomers (EPDM) additives such as slip agents, anti-static agents, colorants, anti-oxidants, stabilizers, fillers, and reinforcers such as CaCO_3 , talc, and glass fiber, and other additives that will be well known to those of ordinary skill in the art.

An R_{ma} of at least 1.1 indicates that an article will exhibit significantly better cold flow, or creep resistance than an article made from a propylene-ethylene copolymer. The greater the R_{ma} number, the more improved the compliance of the

propylene-HAO copolymer in relation to the propylene-ethylene based article. In a preferred embodiment, the R_{ma} is at least 1.2. In a more preferred embodiment, the R_{ma} is at least 1.3.

In addition, to better cold flow resistance, these propylene-HAO copolymers exhibit other improved physical properties. Table I compares physical properties of propylene copolymers of ethylene and propylene copolymers of HAOs and demonstrates that ultimate tensile strength, and impact strength of the propylene-HAO copolymers for example, are significantly improved.

A further indication of the fact that the class of propylene-HAO copolymers is distinct from the propylene-ethylene and propylene-butene propylene copolymer class, is found in the response of the melting points of the copolymers to comonomer incorporation. This is illustrated in Figure 1 It can be seen that the melting point depression for a given molar comonomer incorporation is about twice as much for the propylene-HAO copolymers as for the ethylene and butene resin class of propylene copolymers.

Making Oriented Fibers and Oriented Film

In an embodiment of our invention novel fibers of the present invention may be formed by any method in which a fiber is formed from molten polymer including traditional melt-spinning, of fibers as yarns as well as spunbonding processes, and melt blowing; or by centrifugal spinning, sheet slitting and film fibrillation.

The fiber and subsequently produced fabrics (such as nonwoven fabrics), when made in a typical process from the copolymers of the present invention will generally yield smaller diameter fibers, resulting in a softer fabric. The fibers and fabric will be stronger and exhibit improved resistance to cold flow than a similar fabric made from propylene-ethylene copolymers. These tougher, stronger, creep resistant fibers may be used to make textiles such as knitted woven and nonwoven fabrics. Additionally, fibers made by blending other thermoplastic polymers with a propylene-HAO copolymer and/or fibers made with various additives including, pigments, anti-static agents, antioxidants or other additives are also contemplated.

It is also contemplated that oriented polypropylene film (either uniaxially or biaxially oriented) can be advantageously fabricated from propylene-HAO copolymers of the present invention.

- 13 -

Determination of R_{ms} (Fiber and Fabric Testing)

Creep or cold flow resistance has been discussed above for films, molded articles, tubing, and sheets. For fibers and fabrics, the same physical property is indicative of other physical property step changes. However, the creep or cold flow resistance is measured with a different test.

The creep value of fibers or fiber bundles or fabrics (hereinafter referred to as "fibers") as used in this application is the time of creep under a constant load to a 10% deformation ($t_{10\%}$).

The step change in properties between fiber made from propylene-HAO copolymers and propylene-ethylene copolymers (both being formed in the presence of metallocene catalysts) can be best seen by using a technique similar to that described above for films and other articles.

The technique uses the quotient of the $t_{10\%}$ of a propylene-HAO copolymer, divided by the $t_{10\%}$ of a propylene-ethylene copolymer. The tensile modulus of the fibers should be substantially the same.

The quotient in this instance is given the symbol R_{ms}. Where:

$$R_{ms} = \frac{t_{10\%} \text{ of a propylene-HAO copolymer fiber}}{t_{10\%} \text{ of a propylene-ethylene copolymer fiber}}$$

In the determination of R_{ms}, it is important that substantially all parameters that affect the physical properties of the articles in both the numerator and denominator of the factor be the same.

Such factors include, but are not limited to:

for the resins: molecular weights should vary by no more than 10%

for the fabricated article: fabrication conditions and techniques;

denier of the fiber;

post fabrication treatments;

blend components; or additives

It will be understood by those of ordinary skill in the art that comonomer content of either HAO or ethylene can be varied for purposes of attaining substantially the same tensile modulus in both the propylene-HAO and propylene-ethylene copolymers.

Testing is accomplished as follows:

The fibers samples are conditioned for three days at 22° C and 50% relative

- 14 -

humidity. A predetermined load of 1 g/denier is applied and elongation measured as a function of time.

We contemplate R_{ms} values of at least 1.1, preferably at least 1.2, more preferably at least 1.3. Most preferably at least 1.5.

Example 1

Preparation of Metallocene Catalyst

A silica supported metallocene catalyst was prepared according to the teachings of US Patent No. 5,240,894 using dimethyl silyl, bis(2 methyl, 4,5 benzindenyl) zirconium dichloride as the metallocene as described in Organometallics, v. 13, No. 3, 1994, p. 954-963. The catalyst recipe was 400 grams of silica (Davison 948), 10 grams of metallocene and 3 liters of 10 wt % methyl alumoxane (MAO) in toluene solution. Approximately 600 grams of the finished catalyst system was recovered. This catalyst was prepolymerized with one weight of ethylene per weight of catalyst system at a temperature of 15°C. The ethylene was added over a period of 1.5 hours to assure slow reaction rate.

Example 2

Preparation of Propylene-Ethylene Copolymers

Approximately 15 grams of ethylene and 550 grams of propylene were added to an autoclave maintained at 30°C. After allowing time for equilibration, 0.2 grams of the prepolymerized catalyst of example 1 was added to the reactor and the temperature raised to 50°C over a period of several minutes. An immediate reaction was observed. The reaction was terminated after 30 minutes to limit the extent of conversion of the ethylene so that its concentration in the reaction medium would be nearly constant over the period of the reaction. A total of 114 grams of propylene-ethylene statistical copolymer was obtained. Its weight average molecular weight as measured by size exclusion chromatography was 184,000, its ethylene content (measured by FTIR) was 3.3 wt %, and its peak melting point was 121° C.

Example 3

Preparation of Propylene-1-Hexene Copolymers

To the autoclave of Example 2 was added 550 grams of propylene and 34 grams of hexene-1. The catalyst of Example 1 was added (0.2 grams) and the temperature controlled as in Example 2. The reaction was allowed to run for a

total of two hours in this case since the relative reactivities of propylene and hexene-1 are nearly the same under these conditions. A total of 222 grams of propylene-hexene statistical copolymer was obtained. Its weight average molecular weight as measured by size exclusion chromatography was 204,000, its hexene-1 content was 2.9 wt % (measured by FTIR), and its peak melting point was 126° C.

Example 4 (Prospective Example)

Preparation of Propylene 1-Octene Copolymers

To the autoclave of Example 2, 550 grams of propylene would be added along with approximately 45 grams of 1-octene as the molar amount of Example 3. The catalyst of Example 1 would be added and the temperature would be controlled as in Example 2. The reaction would be allowed to run for 2-3 hours as the reactivities of propylene and 1-octene would be nearly the same under these conditions. Over 200 grams of propylene-octene statistical copolymers could be expected. The average molecular weight as measured by size exclusion chromatography would be over 200,000. The octene-1 content would be expected to be between 2.0 and 4 wt % (if measured by FTIR), and its peak melting point would be in the range of 125-135° C.

Examples 5 and 6

Film Preparation and Testing

These examples show preparation of films from the copolymers of examples 2 and 3 including details of procedures for film forming and property measurement. The data is summarized in Table 1. (Film preparation and testing from a resin produced in Example 4 would follow the same procedures.)

A film of the copolymer to be characterized was formed by compression molding 9.2 grams of the granular copolymer between Mylar® sheets in a form 15 x 15 centimeters in area and 0.5 mm in thickness. The molding procedure was: 1) close the platens (controlled at a temperature of 200° C) until they contact the sample; hold for one minute with no applied pressure; 2) increase the clamping force to 10 Tons and hold for one minute; 3) increase the clamping force to 40 tons and hold for two minutes; 4) release the clamping force and quench the film (still between the Mylar sheets) in a water bath at room temperature. After the films are conditioned for six days at room temperature, dumbbell samples are die-cut from the films.

- 16 -

The tensile properties of the resulting samples were measured on a Zwick REL 2051 tensile tester at a temperature of 25 ± 2 degrees C for the standard tensile properties, procedure DIN 53457 (1987) was adhered to. For the measurement time delayed compliance, the tensile specimen is loaded into the tester just as if one were doing the standard tensile test. A predetermined load is applied and the specimen elongation is recorded as a function of time. The load is chosen to be in the range of 50-60% of that which would cause the specimens to experience yielding (for samples presented here, a load of 11.7 MPa was chosen). The sample elongation recorded 480 seconds after the load is initially applied is chosen as a measure of cold flow for the particular load and this strain divided by the stress applied is designated "the time-delayed compliance".

The results of the evaluation are shown in Table 1.

Example 7 (Prospective Example)

Molded Part Preparation and Testing

The following prospective examples outline expected improvements in molded parts made from propylene-HAO statistical copolymers when compared to either propylene co-polymers made with conventional Ziegler-Natta catalysts or compared to propylene copolymers of propylene and an α -olefin of 4 or less carbon atoms.

The following mechanical properties would be evaluated by the following tests:

In the following examples, mechanical property evaluations were made employing the following tests:

- (1) Melt Flow Rate - ASTM D-1238, Condition L.
- (2) Flexural Modulus, secant - ASTM D-790.
- (3) Shore D Hardness - ASTM D-2240.
- (4) Notched Izod - ASTM D-256.
- (5) Tensile Properties - ASTM D-638.
- (6) Brittleness Temperature - ASTM D-746.
- (7) Vicat Softening Temperature - ASTM D-1525.
- (8) Shrinkage - ASTM D-995.
- (9) Density - ASTM D-2240.

Sample 1 was injection molded in a Van Dorn Model injection molding press into standard parts for the various ASTM tests, then tested for selected mechanical properties.

Example 8 (Prospective Example)**Production of Fibers****FIBER AND FABRIC FORMATION EXAMPLES**

Fibers are prepared as spun, flat (non-lustre or low-lustre), partially oriented yarns (POY) by mechanical take-up of the fiber bundle from its extruded melt. This is accomplished on a fiberline assembled by J. J. Jenkins, Inc. (Stallings, NC). The line consists of a 5 cm (2 inch) Davis Standard Extruder (with 30:1 length/diameter ratio) and 6 cc/rev Zenith metering pump forcing molten polymer through a spinnerette plate of 72 holes of 0.6 mm and 1.2 length/diameter ratio. A metering pump rate of 10 rpm is employed which yields a through-put of 0.625 g/hole/minute.

Fibers were drawn from the 232° C (450° F) melt by an axially spinning unheated godet at 2000 and 2500 m/min. The fiber bundle, expressed as total denier/total filaments collected at each rate is 203/72 and 162/72 respectively. The fiber bundles are collected for characterization as five minute runs by Leesona winder.

The fiber bundle tenacity (g/denier) and elongation are measured by pulling to break on an Instron. Fiber testing is performed on an Instron machine, Model 1122 coupled with the Instron computer which supports the Sintech Sima (Testworks II~) computerized system for material testing. Instron Pneumatic Cord and Yarn Grips (Model 2714) are used for gripping the samples. A sample with 2.5 cm (1 inch) gauge and 0.1 gram preload is pulled at 500 mm/min to break. Break sensitivity is 95% drop in force.

Fibers are melt spun from a 40, 51, and 68 MFR polypropylene. These are materials which were produced by previously described metallocene-type catalysis. Fibers are also spun from a propylene-ethylene random copolymer (Ziegler-Natta catalyzed) which is subjected to controlled rheology treatment (post-reactor oxidative degradation) having 33 MFR (Exxon Chemical Company, PD-9355) and will serve for comparison. The results are obtained from tenacity and elongation testing of those fibers which are spun with take-up rates of 2000 and 2500 m/min.

Example 9 (Prospective Example)**Creep Testing of Fiber Bundles**

Creep experiments would have been performed in a room with controlled atmosphere (20° C, 50% RH) by measuring the fiber bundle elongation versus time

- 18 -

under an applied dead load. The length of the fiber bundle from suspension point to load would be 0.60 m on which gauge length marks of 0.50 m were made after application of a small pre-tension. Dead loads are hung on the fiber bundle corresponding to 20 to 50% of the tenacity g/denier. Creep data are recorded in percent elongation versus time under loads expressed in g/denier. Loads are chosen in order to perform the creep experiments in a practical time, that is within a few hours. Extension is reported as time to creep under a constant load to 10% creep or $t_{10\%}$.

Creep experiments are summarized by parameter: $t_{10\%}$, that is the time required for obtaining a 10% elongation. $T_{10\%}$ is sample and dead load dependent. In order to compare different samples, a constant dead load is ideally used. This is, however, impractical because of the large dependence of creep rate with applied load. More than 2 loads are tested so that creep experiments may be extrapolated to a standard dead load of 1 g/denier.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, films, fibers and molded parts have been exemplified in the present application. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

TABLE I

<u>Polymer</u>	<u>Copolymer of Example 2</u>	<u>Copolymer of Example 3</u>
Tensile Modulus (MPa)	880	900
R_{ma}	1.0	1.68
Tensile Strength (Ultimate - MPa)	38.0	43.7
Dart Impact Strength (Nm/mm)	12.5	14.0
Peak Melting Point (DSC, °C)	121	126

Claims:

1. An article comprised of an isotactic copolymer of propylene and at least one α -olefin, said α -olefin having 5 or more carbon atoms, preferably wherein said α -olefin is selected from the group consisting of 4-methyl-1-pentene, 1-hexene and 1-octene;

said α -olefin being present in said copolymer in the range of from 0.2 to 6 mole percent, preferably 0.5 to 3 mole percent, based on the total moles of monomer in said copolymer, said copolymer having a $M_w/M_n \leq 5$, preferably ≤ 3.5 , said copolymer having a peak melting point in the range of from 100° C to 145° C, preferably wherein said propylene copolymer is produced using a metallocene catalyst system, preferably wherein said metallocene catalyst system contains a silicon bridged bis (substituted 2-methyl-indenyl) zirconium dichloride and methylalumoxane activator; and

wherein an article made from said copolymer has an R_{ms} of at least 1.1, preferably at least 1.2, more preferably at least 1.3.

2. An article as recited in Claim 1 wherein said article further comprises a second polyolefin, wherein said second polyolefin is selected from the group consisting of polyethylene, polypropylene and olefinic elastomers.

3. An article as recited in claim 1 wherein said copolymer further includes a second comonomer, said second comonomer selected from the group consisting of comonomers of from 2 to 20 carbon atoms.

4. The article of claim 1 wherein said article is one of a film, a molded part, tubing or a sheet.

5. An article comprised of an isotactic copolymer of propylene and an α -olefin, said α -olefin having in the range of from 5 to 20 carbon atoms; said α -olefin being present in the range of from 0.5 to 3 mole percent based on the total moles of said copolymer; said copolymer having a $M_w/M_n \leq 3$; wherein said copolymer has a peak melting point in the range of from 115° C to 135° C; wherein a fiber made from said copolymer has an R_{ms} of at least 1.2,

- 20 -

preferably at least 1.3.

6. The article as recited in claim 5 wherein said article is a fabric.

7. An article comprising at least a first isotactic propylene α -olefin copolymer, said α -olefin being one of 4-methyl-1-pentene, 1-hexene and 1-octene;

said propylene, α -olefin copolymer being polymerized by a metallocene-alumoxane catalyst system, wherein said metallocene is dimethyl silyl bis (2-methylbenzindanyl) zirconium dichloride;

wherein said α -olefin is present in the range of from 1 to 3 mole percent based on the total moles of said propylene α -olefin copolymer;

wherein said copolymer has a $M_w/M_n \leq 3$; and

wherein said copolymer has a melting point in the range of from 115° C to 135° C.

8. An article comprising an isotactic copolymer of propylene, a first α -olefin and a second comonomer;

said first α -olefin being one of 4 methyl-1-pentene, 1-hexene and 1-octene;

said second comonomer being one of ethylene, 1-butene, 4-methyl 1-pentene, 1-hexene and 1-octene;

wherein said first α -olefin and said second comonomer are present in said copolymer in a combined total of said first α -olefin and said second comonomer in the range of from 0.2 to 6 mole percent, preferably in the range of 0.5 to 3 mole percent, based on the total moles of said copolymer;

wherein said copolymer has a $M_w/M_n \leq 3.5$;

wherein a film made from said copolymer has an extractable level less than 3 weight percent; and

said film having an R_{ma} of at least 1.2.

9. A fiber comprising an isotactic copolymer of propylene and at least one α -olefin, said α -olefin having 5 or more carbon atoms;

said propylene, α -olefin copolymer made utilizing a metallocene catalyst system, wherein said metallocene is dimethyl silyl bis (2-methyl-benzindanyl) zirconium dichloride;

wherein said α -olefin is present in said copolymer in the range of from 0.5 to 3 mole percent based on the total moles of said copolymer;

- 21 -

wherein said copolymer has a $M_w/M_n \leq 3$;

wherein said copolymer has a melting point in the range of from 100° C to 145° C; and

said fiber having an R_{ms} of at least 1.3.

10. A food container comprising a propylene, α -olefin copolymer, said α -olefin being one of 1-hexene and 1-octene;

said propylene, α -olefin copolymer made utilizing a metallocene catalyst system, wherein said metallocene is dimethyl silyl bis (2-methyl-benzindenyl) zirconium dichloride;

wherein said α -olefin is present in the range of from 1 to 2 mole percent, based on the total moles of said copolymer;

said copolymer has a $M_w/M_n \leq 3$;

said copolymer has a melting point in the range of from 115° C to 135° C; wherein said copolymer is substantially isotactic;

wherein a molded article made from said propylene α -olefin copolymer has an extractable level less than 3 weight percent; and

wherein said molded article has an R_{ma} exceeding 1.3.

11. An article of apparel comprised of fibers, said fibers including an isotactic propylene, α -olefin copolymer, said α -olefin being one of 1-hexene and 1-octene;

said propylene, α -olefin copolymer made utilizing a metallocene catalyst system, wherein said metallocene is dimethyl silyl bis (2-methyl-benzindenyl) zirconium dichloride;

wherein said α -olefin is present in the range of from 1 to 3 mole percent, based on the total moles of said copolymer;

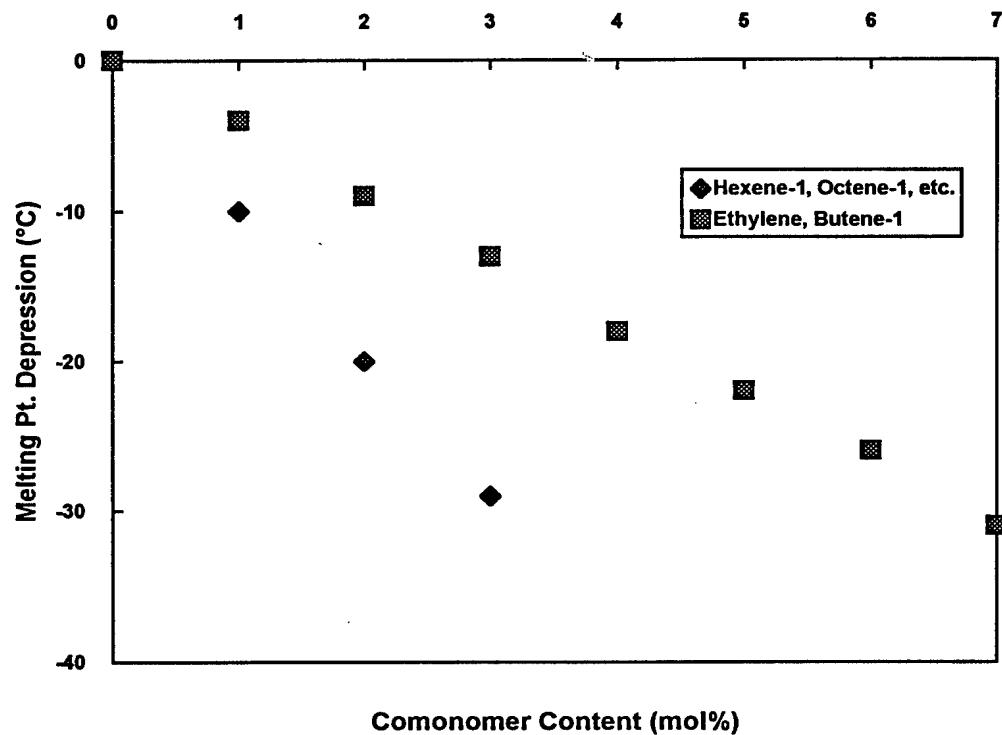
said copolymer has a $M_w/M_n \leq 3$;

said copolymer has a melting point in the range of from 115° C to 135° C; and

said fibers having an R_{ms} exceeding 1.3.

1/1

FIGURE I

EFFECT OF COMONOMER ON MELTING POINT

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/06576

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L23/10 C08J5/18 C08F210/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L C08J C08F D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 384 264 (HOECHST AKTIENGESELLSCHAFT) 29 August 1990 see page 2, line 31 - page 4, line 28; claims; examples 25-27,29; table 7 ----	1-8
Y	US,A,4 461 872 (SU) 24 July 1984 see column 2, line 58 - column 3, line 38; claims -----	9-11
Y		9-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 October 1995	09.10.95
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Clemente Garcia, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 95/06576

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-384264	29-08-90	DE-A-	3904468	16-08-90
		AU-B-	623491	14-05-92
		AU-B-	4939790	23-08-90
		CA-A-	2010064	15-08-90
		JP-A-	3197516	28-08-91
		US-A-	5081322	14-01-92
<hr/>				
US-A-4461872	24-07-84	CA-A-	1222087	19-05-87
		EP-A-	0119508	26-09-84
		JP-A-	59157137	06-09-84
<hr/>				